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Ab initio study of point defects in dielectrics based on Pr oxides

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Abstract

We discuss the influence of band structures and point defects (oxygen vacancies and interstitials, and praseodymium vacancies) in Pr_2O_3, PrO_2, and $PrSiO_{3.5}$ on the electrical properties of high-K gate dielectrics for the application in CMOS technology. In particular, we consider the origin of fixed charges and leakage currents. We address these issues mostly from the perspective of ab initio calculations for formation energies, electronic structures, and band alignment between the film and the silicon substrate.

Keywords: Praseodymium oxide; Silicate; Oxidation state; Point defects; Vacancy; Interstitial; Formation energy; Chemical potential; Charge state; Band offset; Leakage current; Ab initio calculations; Density functional theory

1. Introduction

In the nearest future, a dielectric with a dielectric constant K several times higher than that of SiO_2 will be needed for the fabrication of CMOS (complementary metal–oxide–semiconductor) devices [1]. But despite previous announcements, the industry sticks to SiO_2 as the MOSFET gate dielectric, although this means that the capacitance density cannot be further increased. A major obstacle in the way to substitute SiO_2 by a new material is the need to assure high electrical quality of the dielectric film. At least a part of the problem is associated with the presence of point defects in the new dielectrics. In this work we consider the point defects in the dielectrics based on Pr oxides. While Hf silicate, a material with a moderately high dielectric constant K, appears to be the closest to industrial implementation [2], Pr oxides are among the candidates for truly high-K materials [3]. Pr silicate forms at Pr_2O_3/Si(0 0 1) interfaces in a natural way [4], and it itself is an interesting gate oxide with a moderately high dielectric constant [5,6].

Defects which can trap charge carriers make a contribution to the leakage (through trap-assisted transport of carriers across the film) and/or to mobility degradation of carriers in the channel (through scattering of carriers by the electric field), jeopardizing the gain from the increased dielectric constant. Previous calculations have shown [7,8] that oxygen vacancies in HfO_2 and in ZrO_2 may be responsible for leakages and threshold voltage instabilities. We find that the energy positions of oxygen vacancy charge transition states in Pr oxides are not so critical from the point of view of leakage

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currents as in HfO_2 and ZrO_2, but the concern still remains. We also address the influence of the film stoichiometry (oxygen content in PrO_x) on the leakage current and the role of oxygen interstitials and metal vacancies in the processes responsible for the electrical quality of the film.

2. Approach

Total energy calculations were done with the ab initio plane wave code fhi96md [9,10]. We applied the local density approximation (LDA, [11,12]) and nonlocal pseudopotentials [13,14] with 40 Ry cutoff for plane waves; in some cases, generalized gradient approximation (GGA [15]) was used. The Brillouin zone was sampled at a set of special k-points, akin to the (0.25, 0.25, 0.25) point family generated for cells of dimensions close to these of the Pr_2O_3 unit cell (cube with the lattice constant of $\sim$1 nm).

Because of the open f-shell of Pr atoms, a key problem in calculations involving Pr is the construction of a reliable Pr pseudopotential [16,17]. Our band structure calculations taking into account the whole f-shell of Pr as valence shell have shown that such an approach is unpracticable within LSDA and also within GW. The position of the occupied f-band is much too high and there is no tendency to localize these electrons.

It turns out that in practice two different Pr pseudopotentials are needed: a pseudopotential with two core f electrons for Pr_2O_3 (trivalent PrIII, $+3$ ionic charge), and with only one f electron for PrO_2 (tetravalent PrIV, $+4$ ionic charge). We calibrate the pseudopotential energy difference between PrIII and PrIV in such a way that the experimental difference in the formation enthalpies of Pr_2O_3 and PrO_2 is reproduced [18,19]. The computed lattice constants of Pr_2O_3 and PrO_2 are in agreement with experiment.

The drawback is that the wavefunctions responsible for the $(4+/3+)$ electron transition level of Pr cannot be computed. However, from total energy difference between the perfect crystal and the crystal with one Pr atom in the other charge state one can calculate the energy position of the highest occupied f-band in Pr_2O_3 and $PrSiO_{3.5}$, and the lowest unoccupied f-band in PrO_2. The location of the occupied f-band top is obtained as the $(0/+)$ electron transition state of the isolated f-shell of a Pr atom in the crystal, that is, as the Fermi energy at which the charge state of the Pr atom changes from $+3$ to $+4$. We find these bands at 0.5 above the topmost occupied oxygen states in Pr_2O_3, and at about 0.16 eV below the top of the non-f valence band in $PrSiO_{3.5}$. This is roughly compatible with out XPS measurements, which show the f peak at the valence band top; however, its measured position is typically about 0.5 eV above the position estimated from the calculation. The empty f-band in PrO_2 is computed to be located 1.3 eV above the topmost occupied oxygen states and corresponds to the $(-/0)$ electron transition state of the f shell.

3. Band offsets

Since point defects are usually charged, we must consider the dependence of the defect formation energy G_f on the electron chemical potential, that is, on the Fermi energy E_F. This means that the formation energy of charged defects in a dielectric remaining in electrical contact with the Si substrate is determined by the position of the Fermi level in the substrate and by the valence band offset between Si and the dielectric.

We compute the band offsets (Table 1) using the conjunction that when two materials with an energy gap are brought into contact, their charge neutrality levels (CNLs) tend to match: electrons flow from the

Table 1
Band offsets to Si and charge transition states of oxygen-related defects

	Band offsets to		O_V, energy below CB			O_I, energy above VB
	Si VB	Si CB	$(++/+)$ (eV)	$(+/0)$ (eV)	$(0/-)$ (eV)	$(0/-)$ (eV)
PrO_2	2.6	2.3	0.37	–	–	1.80
Pr_2O_3	2.1	2.1	1.09	0.85	0.21	−0.04
$PrSiO_{3.5}$	2.7	1.8	(*)	(*)	(*)	1.16

For vacancy levels the distance to the conduction band (CB) edge is given, while for interstitial levels the distance to the valence band (VB) edge is specified. For Pr_2O_3, the VB offset and the O_I levels are given with respect to estimated position of f-type VB top. (*) - see text.